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Ag selective electrode based on glassy carbon electrode covered with polyaniline and thiacalix[4]arene as neutral carrier

G.A. Evtugyn *, I.I. Stoikov, S.V. Beljyakova, R.V. Shamagsumova, E.E. Stoikova, A.Yu. Zhukov, I.S. Antipin, H.C. Budnikov

A.M. Butlerov Chemistry Institute, Kazan State University, Kremlevskaya Street 18, Kazan 420008, Russian Federation

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Abstract

Potentiometric sensor based on glassy carbon electrode covered with polyaniline and neutral carrier, e.g. thiacalix[4]arene containing pyridine fragments in the substituents in the lower rim has been developed and applied for determination of Ag^+ ions in the range from 1.0×10^{-2} to 5.0×10^{-7} M with the response time of 12 s. The presence of thiacalixarene in the surface layer improves the reversibility and selectivity of the signal towards transient metal ions. The potentiometric selectivity coefficients were determined for various measurement conditions. As shown, the pH control and the use of NaF as a masking agent fully eliminate the interfering effect of Hg^{2+} and Fe^{3+} ions, respectively. The reaction of Ag^+ with thiacalixarene was proved by the investigation of the extraction of picrate complexes of transient metals in the organic phase. The potentiometric sensor developed was successfully used for the potentiometric determination of silver sulfathiazole (Argosulfan™).

Keywords: Potentiometric sensor; Polyaniline; Calixarene; Host–guest complexation; Silver determination

1. Introduction

Electroconducting polymers are widely applied in the solid-state ion selective electrodes [1,2]. Due to mixed ionic and electronic conductivity, these materials generate electric response to the changes in the content of the potential determining species. The incorporation of conducting polymer into the surface coating of the ion-selective sensor simplifies its manufacture due to the elimination of internal filling and stabilizes the response due to the suppression of the effect of dissolved oxygen and plastic membrane leaching [3]. The thickness, conductivity and charge of the surface layer obtained in electropolymerization are easily controlled by the electrolysis parameters and reaction media content. This makes it possible to change the operational characteristics and analytical performance of the sensors in accordance with the particular tasks of their application. Due to these advantages, the application of electroconductive polymers offers broad opportunities for developing ion-selective electrodes, which are of great importance in chemical, environmental and clinical analysis.

Polyaniline (PANI) [3–6], polythiophene derivatives [7–9] and polypyrrole [10–14] are mainly investigated in the potentiometric sensor development. Generally, the electropolymerized polymer is used either as a solid redox mediator between the transducer and ion-exchangeable component or as an immobilization matrix entrapping the components with intrinsic ionic/electron conductivity. In accordance with this, the sensor potential changes either with the redox potential of the electroconductive polymer or with the number of charged complexes formed by a neutral carrier and guest species on the surface.

Neutral carriers on the calixarene platform are intensively investigated to obtain selective and sensitive recognition response toward various analytes. Simple and cost-effective synthesis, variety of substituents introduced into the lower and upper rims as well as complexation abilities toward inorganic [15–19] and organic [20,21] ions make calixarenes promising components of ion-selective membranes and solid-contact sensors. Most calixarene-based sensors have been developed for selective detection of alkali and alkali-earth metals. Besides, the introduction of soft donor atoms of sulfur and nitrogen into the functional groups of calixarene substituents results in the pri-

* Corresponding author.
E-mail address: Gennady.Evtugyn@ksu.ru (G.A. Evtugyn).

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